

PATENT ABSTRACTS OF JAPAN

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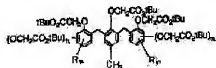
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(54)

2,6-BIS(2-T-BUTOXYCARBONYLMETHYLOXYPHENYLMETHYL)-1-T-BUTOXYCARBONYLMETHYLOXY-4-METHYLBENZENE AND ITS DERIVATIVE



(57)Abstract:

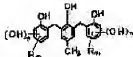
PURPOSE: To obtain the subject compound having a specific mother nucleus structure and t-butoxycarbonylmethyl ether side chains, having high compatibility with polymeric compounds, and useful as a dissolution

I inhibitor for positive resists.

CONSTITUTION: The compound of formula I (R is alkyl; n is 0, 1; m is 0 to 4-n), e.g.

2,6-bis[(2-t-butoxycarbonylmethyloxy-5-methylphenyl)methyl]-1-t-butoxycarbonylmethyloxy-4-methylbenzene. The compound of formula I is preferably obtained e.g. by dissolving a

2,6-bis(2-hydroxyphenylmethyl)-1-hydroxy-4-methylbenzene of formula II, e.g. 2,6-bis[(2-hydroxy-5-methylphenyl)



II methyl-1-hydroxy-4-methylbenzene, in DMF and subsequently reacting the compound of formula II with tbutyl chloroacetate in the presence of potassium carbonate at 60-100° C for 4-8hr, etc.

LEGAL STATUS

[Date of request for examination]

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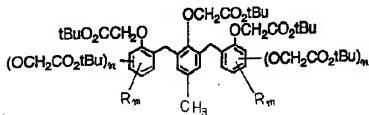
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] 2 expressed with the following-ization 1, 6-bis(2-t-butoxy cull BONIRUMECHIROKISHI
phenylmethyl)-1-t-butoxy cull BONIRUMECHIROKISHI-4-methylbenzene, and its derivative;

[Formula 1]



However, R in ** 1 is an alkyl group, and, in n, 0 or 1, and m express the integer of 0 - 4-n.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the effective new molecular entity as a lysis inhibition agent especially used for positives resist about a new compound.

[0002]

[Description of the Prior Art] Generally performing micro processing, such as a semi-conductor, conventionally using a resist is performed. In this case, in order that resolution may go up so that the radiation of short wavelength, such as high energy ultraviolet rays, an electron ray, and an X-ray, is used and wavelength becomes short, in order to acquire the process tolerance of 0.3 micrometers or less, developing a suitable resist to the radiation of short wavelength more is called for.

[0003] these radiations are used and the so-called chemistry magnification mold resist proposes as one approach for obtaining the resist of high sensitivity and high resolution -- having -- [H.Ito et al., Polym.Eng.Sci., 23 volumes, and 1023 pages (1983)] -- it has been observed. Especially this chemistry magnification mold resist in a positive type ** The two-component system resist which makes an indispensable constituent the high molecular compound which decomposes with an acid and becomes alkali fusibility although it does not dissolve in the compound which absorbs a radiation and generates an acid, and an alkali water solution (JP,2-209977,A etc.), ** The high molecular compound which decomposes with the compound, alkali fusibility high molecular compound, or acid which generates an acid with a radiation, and serves as alkali fusibility. And it is divided roughly into 3 component system resists (JP,2-245756,A etc.) which make an indispensable constituent the lysis inhibition agent which prevents the alkali dissolution of this high molecular compound, and decomposes with an acid, and loses this dissolution stopping power.

[0004] The imaging mechanism of 3 component system resist forms a positive image, when the very small acid which absorbs the irradiated radiation and is generated is made into a catalyst, a chemical reaction occurs in the both sides of a lysis inhibition agent or a lysis inhibition agent, and a high molecular compound and the solubility over the alkali developer of a high molecular compound increases only about the part where the radiation was irradiated by that cause.

[0005] Although very high practical sensibility was realized by the mechanism of such a chemistry magnification mold resist as compared with the conventional resist Since it is spread from [after an alkaline impurity advances from a resist front face and a substrate and irradiates a radiation] before development, an acid deactivates. The part which deactivated had the fault of producing the case where it becomes impossible to dissolve in an alkaline developer, and an exact image cannot be formed even if a radiation is irradiated.

[0006] It originates in this fault and the phenomenon in which a canopy top, such as T top, is formed in a pattern or Susono called skirt length is made to a pattern near a substrate side is observed near the surface of a resist. For this reason, a chemical reaction occurs with the acid for which the radiation was irradiated and which was generated as engine performance required of a lysis inhibition agent, and not only the engine performance of enlarging the dissolution rate ratio of the part by which the radiation was irradiated, and the part which is not irradiated but when membranes are formed as a resist, the engine performance which makes late threshold speed to the inside of the film of an alkaline impurity is also required.

[0007] In order to fill the above-mentioned demand, it is desirable for a lysis inhibition agent to have high compatibility to a high molecular compound, and to have comparatively higher lipophilicity. However, many of lysis inhibition agents [no] announced until now were what can fill these demands completely.

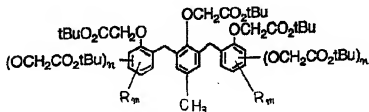
[0008]

[Problem(s) to be Solved by the Invention] Then, when this invention person etc. compounds various compounds, prepares a resist and the engine performance is examined, while finding out a series of mother-nucleus structures excellent in compatibility with a high molecular compound By using the t-butoxy carbonylmethyl ether as a side chain, it found out that contrast with high exposure part and non-irradiating part can be acquired, and that the resistance over penetration of an alkaline impurity could be given, and this invention was reached. Therefore, the purpose of this invention is to offer the effective new compound as a lysis inhibition agent for a positive resist especially.

[0009]

[Means for Solving the Problem] The above-mentioned purpose of this invention was attained by 2 expressed with the following-ization 2, 6-bis(2-t-butoxy cull BONIRUMECIROKISHI phenylmethyl)-1-t-butoxy cull BONIRUMECIROKISHI-4-methylbenzene, and its derivative.

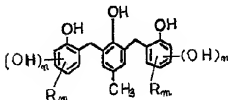
[Formula 2]



However, R in ** 2 is an alkyl group, and, in n, 0 or 1, and m express the integer of 0 - 4-n.

[0010] The compound of this invention is easily compoundable by heating and stirring tert butyl chloroacetate and potassium carbonate moreover, after dissolving 2 expressed with the following-ization 3, and 6-bis(2-hydroxy phenylmethyl)-1-hydroxy-4-methylbenzene, or its derivative in a suitable solvent.

[Formula 3]



[0011] As an example of R, although a methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, an isobutyl radical, t-butyl, a pentyl radical, a neopentyl radical, a hexyl group, etc. can be mentioned, for example, a methyl group and an ethyl group are desirable also especially in these. Moreover, 0 or 1, and m of n are 0 - 4-n As a solvent used at the time of composition, although DMF, DMSO, an acetone, etc. can be mentioned, it is desirable to use DMF also especially in these.

[0012] moreover, tert butyl chloroacetate -- or although it can change to it and bromoacetic acid-t-butyl,

iodoacetic acid-t-butyl, etc. can also be used, it is desirable to use tert butyl chloroacetate from viewpoints, such as acquisition ease, handling nature, and reactivity, the same — potassium carbonate — or although it can change to potassium carbonate and a sodium carbonate, a lithium carbonate, etc. can also be used, it is desirable to use potassium carbonate or a sodium carbonate especially from viewpoints, such as reactivity.

[0013] Especially as long as the amount of these reactants used is more than the amount of theory that needs tert butyl chloroacetate, potassium carbonate, etc. to obtain the specified substance, it is not restricted, but since the above-mentioned reaction advances quantitatively, use of the amount of theory is sufficient.

Although a reaction is performed stirring among 40 degrees C - 120 degrees C, it is desirable from a viewpoint of reaction time and yield to make it react at 60 degrees C - 100 degrees C especially, and, as for the concentration of reaction mixture, it is desirable that it is 10 % of the weight - 50 % of the weight. If it is these reaction conditions, a reaction will be ended in 4 hours - 8 hours. It can perform easily carrying out separation *** of the specified substance from the reaction mixture after reaction termination by combining a well-known approach suitably.

[0014] Since the compound of this invention is easily desorbed from a t-butoxy carbonylmethyl ether group and becomes alkali fusibility under existence of an acid while it has the mother-nucleus structure excellent in compatibility with a high molecular compound, it is especially effective as a lysis inhibition agent of the positive-resist ingredient of 3 component system. The positive-resist ingredient of 3 component system is constituted by (A) lysis inhibition agent, the (B) acid generator, the (C) high molecular compound, and the (D) solvent like common knowledge. In this case, the weight ratio of A:B:C:D is 5-50:0.5-30:70-90:150-700, and is 10-25:2-8:75-85:250-500 preferably.

[0015]

[Effect of the Invention] Since the compound of this invention has high compatibility to a high molecular compound, it can be used in large quantities as a dissolution inhibitor into 3 component positive resist. Moreover, since lipophilicity is high, it has the effectiveness which an alkali impurity makes it hard to advance into the resist film from a resist front-face and substrate side.

[0016]

[Example] Hereafter, this invention is not limited by this although an example explains this invention to a detail further.

an example 1.2 and 6-screw [(2-hydroxy-5-methylphenyl) methyl]-1-hydroxy-4-methylbenzene 3.5g (0.01 mols) — DMF50g — dissolving — 4.5g (0.03 mols) of tert butyls chloroacetate, and 4.1g (0.03 mols) of potassium carbonate — in addition, 6-hour heating and stirring of were done at 80 degrees C.

[0017] After adding and washing 100g of water further to the toluene phase which added toluene 50g and 100g of water, and was separated after cooling reaction mixture radiationally and drying with magnesium sulfate, when reduced pressure distilling off of the solvent was carried out, the oil-like reaction mixture was obtained.

When the silica gel column chromatography (elution solvent: chloroform) refined this, 2 and 6-screw [(2-t-butoxy cull BONIRUMECHIROKISHI-5-methylphenyl) methyl]-1-t-butoxy cull BONIRUMECHIROKISHI-4-methylbenzene 5.2g (76% of yield) were obtained as colorless oil.

[0018] Following It was checked from delta value of $^1\text{H-NMR}$, and the result of elemental analysis that it is the above-mentioned compound.

$^1\text{H-NMR}$ delta 1.47 (s18H and t-bu-CH₃) and delta 1.49 (s9H and t-bu-CH₃)

delta2.13 (s3H and Ph-CH3), delta2.22 (s6H and Ph-CH3), delta4.06 (s4H and Ph2-CH2), delta4.30 (s2H and -OCH2 CO), delta4.49 (s4H and -OCH2 CO), delta6.63 (d2H, Ph-H), delta6.73 (s2H, Ph-H), delta6.91 (m4H, Ph-H)

Elemental-analysis analysis value (%) C:71.57, H:8.09 theoretical-value (%) C:71.28, H:7.88 [0019] an example 2.2 and 6-screw [(2, 4-dihydroxy-3-methylphenyl) methyl]-1-hydroxy-4-methylbenzene 3.8g (0.01 mols) -- DMF50g -- dissolving -- 7.5g (0.05 mols) of tert butyls chloroacetate, and 6.9g (0.05 mols) of potassium carbonate -- in addition, 6-hour heating and stirring of were done at 100 degrees C, and also 5.0g of colorless oil was obtained completely like the example 1. The result of the obtained oily nature matter, 1 H-NMR spectrum, and elemental analysis is as follows.

[0020] delta1.42 (s9H and t-bu-CH3) and delta1.46 (s18H --) t-bu-CH3, delta 1.48 (s18H and t-bu-CH3), delta2.12 (s3H and Ph-CH3), delta2.24 (s6H and Ph-CH3), delta4.02 (s4H and Ph2-CH2), delta4.24 (s6H and -OCH2 CO), delta4.48 (s4H and -OCH2 CO), delta6.02 (d2H, Ph-H), delta6.62 (s2H, Ph-H), delta6.78 (s2H, Ph-H)

Elemental-analysis analysis value (%) It was checked from the result of C:67.31, H:8.01 theoretical-value (%) C:66.93, and H:7.84 analysis that the obtained compounds are 2 and 6-screw [(2 or 4G t-butoxy cull BONIRUMECHIROKISHI-3-methylphenyl) methyl]-1-t-butoxy cull BONIRUMECHIROKISHI-4-methylbenzene. In addition, yield was 53%.

[Translation done.]